Indian J. Phys. **49**, 746 756 (1975)

Compressibility of molecular organic compounds*

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(*Received* 16 *November* 1974, *revised* 7 *May* 1975)

The compressibility of a number of aromatic crystalline hydrocarbons, napthalene, anthracene, biphenyl, *p*-terphenyl and substituted benzenes, *p*-dichlorobenzene and benzophenone have been measured to pressures of 35 kilobars Our new determinations of compressibility agree remarkably well with the determinations to 12 kilobars by Kabalkina In general present results show compressions from 10% to 25% less than those reported by Bridgman

1. Introduction

The compressibilities of a number of aromatic crystalline hydrocarbons, napthalene, anthracene, biphenyl, *p*-terphenyl, and substituted benzenes, have been studied by Bridgman (1945, 1948. 1949) and Kabalkina (1962) These crystals all have a monoclinic unit cell containing two molecules, one at the corner and the other at the center of the *ab* face The crystal structure is described by the symmetry classification $C_{2h}{}^5$ Benzophenone belongs to the space group $P^2{}_1{}^2{}_1{}^2{}_1$ and has orthorhombic symmetry Four molecules are included in the unit cell At room temperature, these compounds exist in the form of crystalline solids

2 Pressure Induced Structurae Changes

Molecular crystals have properties sensitive to both the crystal geometry and magnitude of the overlap, it is necessary to have some measure of the pressure induced intermolecular and intramolecular structural changes We consider here some qualitative arguments which suffice to define the order of magnitude of the expected effects A system characterised by a constant isothermal compressibility, k, the isothermal equation of state is

$$V = V_0 \exp(-kp), \qquad \ldots \quad (1)$$

where V_0 is the volume at zero pressure and V is the volume at pressure p and the compression work W, per molecule is

$$W = \int p dv = V_0 \{1/k\,(1-\exp(-kp)-p \exp(-kp)\}, \qquad \ldots \quad (2)$$

*This work was done in the Laboratory of Prof. G. C. Kennedy, Institute of Geophysis and Planetary Physics, University of California, Los Angeles.

which for $kp \ll 1$ reduce to $W = KV_0p^2$. For molecular crystals, we take the average zero pressure volume to be $V_0 = 50\text{Å}^3$ and the compressibility to be of the order of 10^{-6} atm^{-1}. From the data, $(W/eV) \sim 10^{-6}(p/atm)^2$(for $kp \ll 1$). This order of magnitude estimate indicates that for pressure upto 10^5 atm, $W \leqslant 0.01$eV, so that only the lattice dimension will be affected by the compression. In the pressure region $p \geqslant 3 \times 10^5$ atm, the compression work computed by eq. (2) is $W \geqslant 0.1$eV, i.e., of the order of magnitude of intermolecular interactions between aromatic molecules.

Kabalkina (1962) recently obtained the linear compressibility data for biphenyl, terphenyl, quaterphenyl, napthalene and anthracene in the pressure range (1-15000 kg/cm^2) by X-ray method. She determined the linear compressibility data $\Delta a/a$, $\Delta b/b$, $\Delta c/c$, and cotg $\beta\Delta\beta$ for monoclinic molecular crystals as function of pressures, where a, b, and c are the unit cell dimensions and Δa, Δb, and Δc, are the changes in the unit cell dimensions due to compression. From these data, the values of $\Delta V/V_0$ were evaluated by using the analytical expression

$$\Delta V/V_0 = \Delta a/a + \Delta b/b + \Delta c/c + \text{cotg}\,\beta\Delta\beta \qquad \ldots \quad (3)$$

Bridgman (1948) had previously determined the values of V/V_0 by direct measurements of compressibility using a piston displacement technique.

3 Experimental Procedure

The experimental technique used in these measurements is sharply different from that of Bridgman although Bridgman also used a piston displacement technique. He observed piston motion in a double stage system, observing changes of resistance of a slide wire potentiometer and his pressure measurement was indirect. In addition, our sample sizes were very much larger. Bridgman's measurements of compressibilities of organic compounds were on samples of the order of 0.1 cc, whereas our sample occupies a volume of approximately $\frac{1}{2}'' \times 1\frac{1}{2}''$. Thin lead foil was wrapped around the sample in order to minimize friction between sample and inner wall of the carbaloy container. Figure 1 shows the general arrangement of the pressure cell and the sample.

The compressibility of our samples was determined by observing displacement of a tungsten carbide piston.

This piston displacement was read on a dial gauge graduated to record 0.001″ division. The oil pressure of the ram which drove the piston was read on a Heise Bourdon tube gauge. The accuracy of the pressure reading was to ± 0.5 bar. This corresponded to an uncertainty of ± 1.36kb pressure in the actual pressure as seen by the sample. Piston displacement was recorded during the compression and the decompression of the sample. True pressure was computed from the arithmatic mean of the two readings. This takes into account both piston friction

and the frictitional pressure between the container wall and the sample. It was necessary to make corrections for the shortening of the piston, dilatation of the cross section of the core, and compression of the pyrophyllite sealing rings and steel discs Thus, experiments were made to determines the compressibility of gold by piston displacement technique. Bridgman has scarefully measured the compressibilityof gold. The compressibility of gold is small in comparison to the compressibility of organic solids and the uncertainty in the compressibility of gold is correspondingly small. The total correction factor in our measurements was derived by taking the difference between our experimental and Bridgman's values for $\Delta V/V_0$ for gold Thus all our data are tied to Bridgman's values for gold.

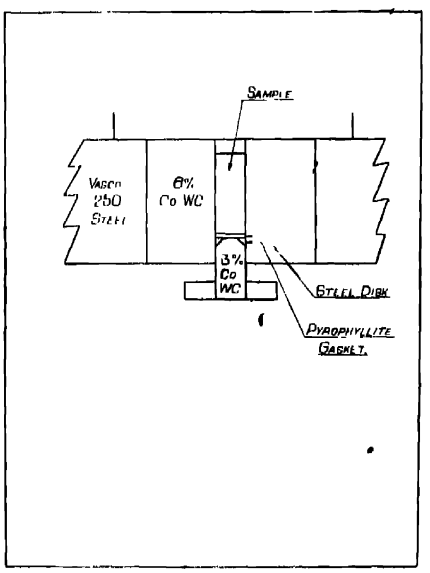

Fig. 1. Arrangement of pressure cell and sample

Samples of well geometrical configurations were prepared by pressing the powder crystals in the form of a cylindrical rod The pressure cycling process was repeated until the sample showed the same value of compression for subsequent pressure-cycles. The dimensions of the rods were about 1 6 inches in length and 0 496 inches in diameter Each sample was weighed to know the mass. From these two data i.e . volume and mass, the density of each sample was determined These values of densities were found to agree well with those obtained from I C T Initial volumes of the samples studied were determined by (i) measuring the geometrical dimensions of the samples used and (ii) measuring the mass of the samples and taking the values of density from I C.T Thus the initial volumes of the samples were checked in both ways. Here the initial sample volume was taken

to be that volume which was attained after repeating the pressure cycles until the sample gave the same values of compression for the subsequent pressure cycling process. The data, as obtained by the above mentioned two methods, on the initial volume of the sample agree well.

For some runs automatic recordings of the piston displacement against pressure were made on an $x-y$ recorder (Mosely Autograf) along with the direct reading from the dial gauges. A BLH strain gauge model SR4 pressure cell capacity 10,000 psi, was incorporated in series with the Heise gauge. The output of the strain gauge was amplified by D. C. amplifier, model No. 425A and fed into the X-terminals of the recorder. An optical device was pioneered by the author in these investigations for recording the piston displacement. The linear motion of the cylinder driving the piston was coupled mechanically to a pair of guided plates covering an optical slit 1″ in length and 1/8″ in width located in front of a RCA 925 photocell. This slit was illuminated by a 100W projector lamp. During the compression and decompression cycle, the pair of plates moved simultaneously to close and to open the slit. The geometry of the slit was adjusted to make the output of the photocell linear with piston motion. The output of the photocell was applied to the y-terminals of the recorder. This optical device was found to be superior to linear potentiometric devices. These two devices for estimating the piston displacements were used as auxiliary means and to detect any irregularity in the piston displacement due to some phase transformation and other characteristic changes in the sample. But in these investigations no significant irregularities were observed. As these two devices were calibrated in terms of piston displacement parameter, we have considered the dial reading data to record the estimate of the piston displacement.

All the experiments were carried out at room temperature (22-24°C). In practice it was found that these organic materials needed to be cycled from 0 to 40 kbar six to eight times before reproducible values of $\Delta V/V_0$ could be obtained.

Materials studied

Tables 1 and 2 show some of the physical constants of the molecular crystals studied. Biphenyl, naphthalene, *p*-dichlorobenzene and benzophenone were obtained from J. T. Baker Chemical and specified as analytical quality. *p*-terphenyl and anthracene were obtained from Matheson Coleman and Bell and specified as scintillation quality. Following tables are presented here to show the additional informations about the crystals as guide to these investigations. Table 3 shows the typical changes in unit cell of crystals of linear poly phenyls at $p = 10^4 \text{kg/cm}^2$. Table 4 shows the fractional pressure induced volume changes for a model crystal of aromatic crystals as extrapolated by Samara & Drickamer (1962) from Bridgeman's data.

In table 5 the extrapolated data as obtained by the combination of the general compressibility data (Table 4) with the biphenyl linear compressibility data to

construct the general linear compressibility curve for monoclinic crystals are displayed to give a reasonable approximation to the change in the unit cell dimensions of monoclinic crystals.

Table 1, Molecular constants of the substances studied

Name	Chemical formula	Molecular weight	M P. °C	B P. °C	density g/c.c
Biphenyl	$(C_6H_5 \cdot C_6H_5)$	154.08	69 0	254.9	1 041
p-Terphenyl	$(C_6H_5)_2C_6H_4$	230 29	213	—	1.234
Napthalene	$(C_{10}H_8)$	128.2	80.1	217 9	1.145
Anthracene	$(C_6H_4 \cdot (CH)_2 \cdot C_6H_4)$	178.22	217	354 5	1 25
p-Dichloro-benzene	$(C_6H_4Cl_2)$	146 95	52.9	173	1 458
Benzophenone	$(C_6H_5CO_6H_5)$	182 08	48 5	305.4	1 08

Table 2. Crystal constants at zero pressure

	a	*b*	*c*	β	System
Napthalene[1]	8 235Å	6 003Å	8.658°	122°55′	Monoclinic
Anthracene[2]	8.561Å	6 030Å	11.163Å	124°42	,,
Biphenyl[3]	8 12±0.02Å	5.63±0.01Å	9.51±0 02Å	95 1°±0.03°	,,
Terphendl[4]	8 08Å	5.60Å	13.59Å	91°55′	,,
p-dichloro-benzene[5]	14.83Å	5.88Å	4.10Å	112°30′	,,
Benzophenone[6]	10 30Å	12.11Å	8 04Å		Orthorhombic

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Table 3. Changes in unit cell dimensions of crystals of linear polyphenyls at $p = 10^4 kg/cm^2$

Crystals	$\Delta a/a$	$\Delta b/b$	$\Delta c/c$	Cotg $\beta\Delta\beta$
Biphenyl	0 054±0.002	0 030±0 002	0 022	0.002±0 002
Terphenyl	0 054 0.002	0.030±0 002	0 014	−0.002±0 002

Available linear compressibility data are listed in table 3

Table 4. Fractional pressure induced volume changes for a model crystal of aromatic molecules. (Extrapolated by Samara & Drickamer (1962) from Bridgeman's Data)

Pressure 10^3 bar	$\Delta V/V_0$
10	0.095
20	0.133
40	0.190
60	0.227
80	0.255
100	0.276
140	0.303
180	0.319
200	0.324
240	0.328
280	0.330
300	0.331

The fractional pressure induced volume changes in a monoclinic crystal are given by the eq (2) which is $\Delta V/V_0 = \Delta a/a + \Delta b/c + \Delta c/c + \cot g\beta\Delta\beta$.

Assuming that the ratios $\Delta a/a$, $\Delta b/b$, $\Delta c/c$, $\Delta\beta/\beta$ are pressure independent, the general volume compressibility data (table 4) may be combined with the biphenyl linear compressibility data to construct a general linear compressibility cue for monoclinic crystals These extrapolated data displayed in table 5, should give a reasonable anproximation to the change in the unit cell dimensions of monoclinic molecular crystals such as napthalene, anthracene and the linear polyphenyls, and should serve as a starting point for the computation of pressure effects on the electronic states of these systems.

Biphenyl: The corrected values of $\Delta V/V_0$ are plotted against pressure in figure 2 The values of $\Delta V/V_0$as obsained by Bridgman (1949) and Kabalkina (1962) are also shown in the figure for comparison. In the low pressure region data obtained by Kabalkina and that obtained in this investigation are in agreement. The data obtained by Bridgman also agree well with the present data in the low pressure region. Bridgman's data differ by a large amount in the high pressure region. At 35kb, about 15.2% compression was observed,

Table 5 Linear compressibility data for a model monoclinic crystal

10^3 bar	$\Delta a/a$	$\Delta b/b$	$\Delta c/c$
10	0 054	0 030	0.020
20	0 072	0 040	0 027
40	0 103	0 058	0 038
60	0 123	0 068	0 045
80	0 137	0 076	0 051
100	0.149	0 082	0 055
140	0 164	0 091	0 061
200	0.175	0 097	0 065
240	0 177	0.098	0 066
300	0 178	0 099	0 067

Table 6 Experimentally determined compressibility of the following organic molecules, $\Delta V/V_0$

Kbars	5	10	15	20	25	30	35
Biphenyl	0 054	0 085	0 107	0 122	0 135	0 144	0 152
p-Terphenyl	0.053	0 089	0 110	0 126	0 139	0 148	01 54
Napthalene	0 048	0 082	0 106	0126	0 142	0 155	0 165
Anthracene	0 044	0 078	0 102	0 120	0.134	0 144	0 152
p-Dichloro-benzene	0 045	0 075	0 097	0 113	0 128	0 139	0 150
Benzophenone	0 040	0 072	0 095	0 112	0 123	0 134	0 140

The results obtained are shown in a summarised way in table 6

p-Terphenyl Our values of $\Delta V/V_0$ as well as results from Bridgman and Kabalkina are plotted against pressure in figure 3 The agreement between our data and that obtained by Kabalkina is excellent. At 35kb, about 15.2% compression was observed.

Napthalene The various results on $\Delta V/V_0$ are shown in figure 4 Our agreement with Kabalkina is satisfactory At 35 kb, about 15.2% compression was observed.

Anthracene The various results on $\Delta V/V_0$ are plotted in figure 5. Again our data and Kabalkina's data are in excellent agreement. There is a large discrepancy at higher pressure between the Bridgman data and our results. At 35 kb total compression is about 15.2%.

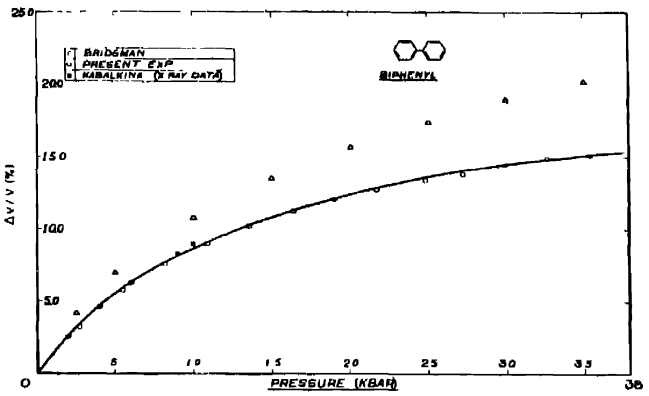

Fig 2

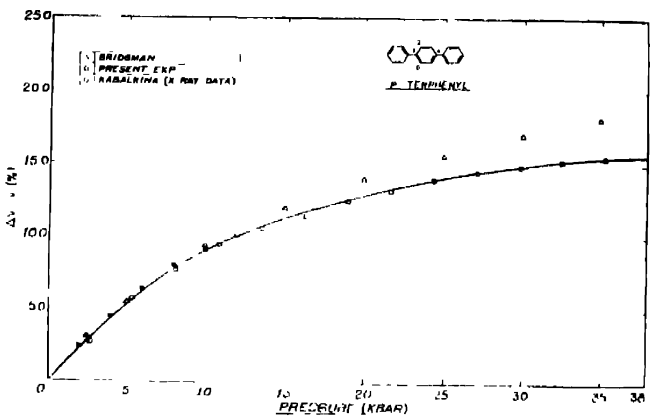

Fig 3

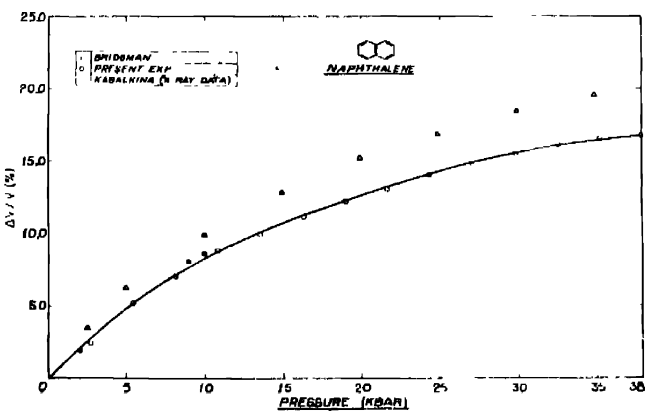

Fig. 4

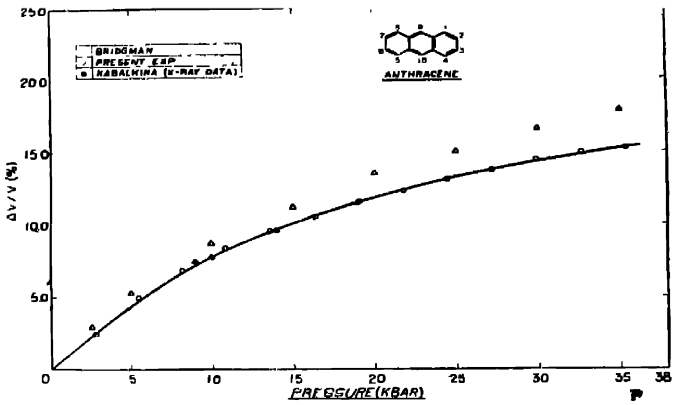

Fig. 5

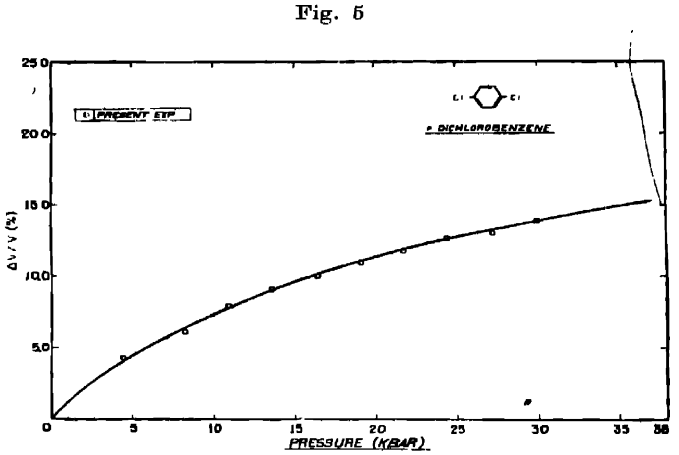

Fig. 6

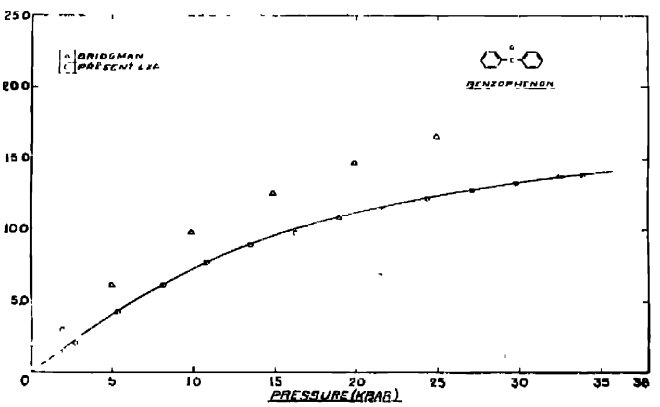

Fig. 7

p-Dichlorobenzene : Our results on $\Delta V/V_0$ are plotted against pressure in figure 6 At 35 kb. 15 0% compression was observed.

Benzophenons : Our results on $\Delta V/V_0$ are plotted against pressure in figure 7. At 35 kb, about 14 04% compression was observed

5. Discussion

Covalent interaction between atoms of a mlecule and weak Van der Waals interaction between molecules are the two well known interactions that occur in molecular crystals. Under high compression, the intermolecular distances are shortened. The compressibilities of the substances depend on the numerical ratio of covalent and Van der Waals bonds in the unit cell. Kabalkina's X-ray data on biphenyl, terphényl, quaterphenyl, napthalene and anthracene, provide information regarding the changes under pressure in the unit cell dimensions. Since the molecular crystals of aromatic molecules are held together by dispersion forces and because these intermolecular interactions are weak, the crystals are expected to be quite compressible in the pressure range upto 100 kb. The X-ray method is sensitive enough to detect small changes in unit cell dimensions. We have carried out the measurement on the compressibilities of the molecular crystals by static compression technique upto 35kb Our results, using gold as a reference standard, have been found found to agree well with the X-ray data by Kabalkina, where the data overlap Kabalkina's investigations extend only upto 15,000 Kg/cms. There is a surprisingly large discrepancy between Bridgman's data and our data. Bridgman obtained his values of $\Delta V/V_0$ by subtracting the compressibiliey of the piston and the steel sealing ring but ignored dilation of his carbide pressure vessel. However, at high pressure the carbide pressure vessel dilates and the supporting steel cylinders alter in dimensions. This may be one of the major reasons for the difference in the two sets of results

In the case of *p*-dichlorobenzene, Bridgman observed a transition in the neighbourhood of 23,000 Kg/cm° at 50°C, 30,000 at 100°C and 38,000 at 150°C By extrapolating Bridgman's data, it appears that at room temperature a transition should occur at 20 kb. However, in the present experiments, no significant change in volume was detected at this pressure In seasoned samples no irregularities as indicated by Bridgman, were observed. Our results clearly indicates the significance of seasoning the samples and consequently compression (10-25%) less than those reported by Bridgman, are obtained in the present investimations.

From the Table 3, it is evident that the values of compression at 35kb for the samples studied agree very well i.e., the sample to sample difference in compression values is negligibly small

ACKNOWLEDGMENT

The author is thankful to Prof, G. C. Kennedy for his interest and valuable discussions.

Partial financial support from National Science Foundation Grant GA 640 is gratefully acknowledged.

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